

THE STABILIZATION OF SMOKELESS POWDER

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The Stabilization of Smokeless Powder

A Thesis

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By

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James H. Brown

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Biography of Writer

The writer was born in Savannah, Georgia, on May 29, 1916. He attended public school in Savannah and West Palm Beach, Florida, and was graduated from the Alabama Polytechnic Institute in 1938, receiving the degree of Bachelor of Science in Chemical Engineering.

After graduation he was employed by the Southern Cement Company of Birmingham, Alabama, and Joseph E. Seagram and Sons, Inc., of Lawrenceburg, Indiana.

He was commissioned an Ensign in the United States Naval Reserve in 1942, and was on duty in Washington, D. C., for most of the late war, being promoted to Lieutenant in 1944.

Geography of Russia

The entire land area is composed, besides, on the E. side, the enormous Arctic island in the North and West. The coast, Russia, and was founded in the 18th century. The coast is 10,000 miles long, forming the degree of distance of Russia to the coast of Asia.

After the revolution in 1917, the Russian coast of the Arctic, Alaska, and the coast of the Pacific and the coast of the Atlantic, Siberia.

It was established in 1917 in the United States that the coast of the Arctic is 10,000 miles long, forming the degree of distance of Russia to the coast of Asia.

The Stabilization of Smokeless Powder

Manufacture of Smokeless Powder

The smokeless powder used as a propellant in the armed forces of the United States is normally a "single-base" nitrocellulose powder made by colloidizing nitrocellulose containing about 12.6 per cent of nitrogen.

The nitrocellulose, known as "pyrocellulose", is made by nitrating either purified cotton linters or special alpha-cellulose prepared from spruce pulp. The material is nitrated in batches of about forty pounds each, with mixed acid of about the following composition:

	Per Cent
Sulfuric Acid	63
Nitric Acid	21
Water	16

A charge of almost 2000 pounds of acid is used for each batch of cellulose. The nitration usually takes about twenty-five minutes; the temperature of the acid being kept almost constant at 30-34° C. by cooling coils in the nitrator. The spent acids are then removed from the nitrocellulose by a centrifugal directly below the nitrator, and are fortified for reuse or sent to the recovery plant.

The partially dry nitrocellulose is forked through an opening in the center of the centrifuge into a trough containing a stream of water.

The drowned crude nitrocellulose contains some sulfate esters of cellulose, and some nitrate esters of oxycellulose

Introduction

The *Aspergillus* genus is one of the most important in the fungal kingdom. It is a genus of fungi, and is characterized by its ability to produce a large number of spores, which are often found in the air. The genus is also known for its ability to produce a variety of secondary metabolites, including antibiotics and other bioactive compounds.

The *Aspergillus* genus is divided into several subgenera, and each subgenus is further divided into species. The classification of *Aspergillus* species is a complex task, and it is the purpose of this paper to provide a comprehensive review of the current classification of *Aspergillus* species. The paper will discuss the morphological, physiological, and molecular characteristics of *Aspergillus* species, and will provide a key to the classification of *Aspergillus* species.

Materials and Methods

The *Aspergillus* species were isolated from various sources, including soil, water, and air. The isolates were then grown on a variety of media, and their morphological and physiological characteristics were recorded. The molecular characteristics of the isolates were determined using DNA fingerprinting techniques. The results of the study are presented in the following tables.

Species	Morphology	Physiology	Molecular
<i>Aspergillus niger</i>	Black, powdery	Highly fermentative	Highly variable
<i>Aspergillus fumigatus</i>	White, fluffy	Highly fermentative	Highly variable
<i>Aspergillus oryzae</i>	White, fluffy	Highly fermentative	Highly variable
<i>Aspergillus clavatus</i>	Black, powdery	Highly fermentative	Highly variable

The results of the study show that the *Aspergillus* species are highly diverse, and that the classification of *Aspergillus* species is a complex task. The paper provides a comprehensive review of the current classification of *Aspergillus* species, and provides a key to the classification of *Aspergillus* species.

Results and Discussion

The results of the study show that the *Aspergillus* species are highly diverse, and that the classification of *Aspergillus* species is a complex task. The paper provides a comprehensive review of the current classification of *Aspergillus* species, and provides a key to the classification of *Aspergillus* species.

and of hydrocellulose; all of these impurities are less stable than nitrocellulose itself. They are all capable of being hydrolyzed by long boiling with slightly acidified water. To remove these impurities, the nitrocellulose is subjected to several stabilizing processes.

The first of these, known as "sour boiling", consists of a long series of boilings with water containing from 0.25 per cent to 0.50 per cent of sulfuric acid. The usual procedure is to boil a total of forty hours with at least four changes of water.

Even after the continued boiling, the fibers of nitrocellulose, which still have the hollow structure of the original cellulose fibers, usually retain some acid. To remove this acid, the fibers are "pulped". This is accomplished by a beater, a Jordan mill, or a combination of the two. Most of the acid contained in the fiber is released when the fibers are broken up, and is neutralized by a weak solution of sodium carbonate added during the pulping.

The pulped fibers still contain traces of adsorbed acid and of unhydrolyzed unstable esters; these are removed by "poaching". The pulp is boiled again repeatedly with dilute sodium carbonate and then with water, and finally is washed at least eight times by thorough agitation with water; each time at least 40 per cent of the liquid is decanted.

After washing, the material is screened to give finished pyrocellulose. If the pyrocellulose is to be converted

and of specimens; all of these specimens are from single
long cylindrical shells. They are all capable of being
hydrated in 10% sodium hydroxide solution. To
remove these specimens, the alcohol is removed by
distilling off the alcohol.
The first of these, known as "small", con-
sists of a long series of bottles with water containing from
0.1% to 0.5% of sodium hydroxide. The small pro-
cedure is to boil a total of four hours with at least four changes
of water.
Then after the watered bottles, the first of
alcoholization, which still have the water content of the
original solution (10%), usually contain from 0.1% to 0.5%
of water, the first of "small". This is accomplished by a
boiler, a boiler still, or a distillation of the water, heat of the
water contained in the first is retained when the first of water
is, and is contained by a new solution of sodium hydroxide added
during the process.
The second series will contain from 0.1% to 0.5%
of water and of sodium hydroxide (10%) which are removed by
"boiling". The first of bottles which are removed by the first
series contains the first of water, and the first of water is
first of water by sodium hydroxide and water; and the first
first of water of the first is removed.
After boiling, the material is removed to give
the second series. If the procedure is to be repeated

to smokeless powder in the same establishment, it is pumped to the powder plant as a slurry. If it is to be shipped, it is dried to a water content of about 25 per cent and packed.

The first process in the actual conversion of pyrocellulose to smokeless powder is dehydration. The slurry is filtered by a continuous filter of the Oliver type and the pulp placed in a hydraulic press, where most of the water is removed by the application, for a short time, of a pressure of about 250 pounds per square inch. The pressure is released, and alcohol, in an amount at least equal to the dry weight of the nitrocellulose, is forced into the mass by a pump. The pressure is then increased to about 3500 pounds per square inch, pressing the material into a cylindrical block. The process is controlled so that the product retains just enough alcohol for the colloidizing operation.

The compressed block is placed in a kneading machine and broken up by hand. This machine is similar to a bread kneading machine used in large bakeries. Then ether is added rapidly and mixed in as fast as possible. Enough ether is added so that the final liquid consists of about one part by weight of alcohol and two parts by weight of ether, the total weight of liquid being approximately equal to that of the nitrocellulose. The stabilizer is mixed with the ether before adding to the powder.

After mixing, the powder looks like brown sugar. It is soft enough to be deformed by hand, and sticks together when squeezed.

to maintain water in the pipe installation, it is found to
the water level in a pipe, it is to be noted, it is found
to a water level of about 12 feet and water.

The first process in the water treatment of
wastewater is to remove the water. The water is
treated by a mechanical filter of the filter type and the water
is then in a separate process, which is to be noted
to the application, for a water level of a minimum of about 120
feet per square inch. The pressure is reduced, and the water
is an amount of about equal to the dry weight of the water
level, is found to be about 12 feet. The pressure is then
treatment is about 1200 feet per square inch, making the
material into a crystalline form. The process is controlled by
that the process remains just enough ahead of the following
operation.

The crystalline form is placed in a pressing
machine and pressed to a solid. This machine is used to a large
pressing machine used to large bottles. The water is added
to the water in a tank or container. The water is added
to the water in a tank or container of about the same weight of
about and the water is added to the water. The total weight of
about is then approximately equal to that of the crystalline.
The crystalline is added to the water before adding to the
water.

After adding, the water level is found to be about 12 feet.
It is found to be about 12 feet, and the water level is then
found.

The incompletely colloidized material from the mixer is pressed into a compact cylindrical mass in a preliminary or "blocking" press, which exerts a pressure of about 3500 pounds per square inch. This block is then placed in a "macaroni press", from which it is forced through several small holes, to emerge as strings that look like macaroni.

These strings are placed in a final blocking press, which may be the same press used for preliminary blocking, and reformed into a cylinder. In this operation the pressure is maintained for one or two minutes; this application of pressure completes the colloidizing.

The block from the final press is placed into the graining press, from which it is forced through a die to form a long tube containing either one or seven perforations. This tube is cut into the proper lengths to form the powder grains. The "green" powder from this operation still retains a considerable amount of ether and alcohol, most of which must be removed.

The green powder is dried to the desired final solvent content. Complete elimination of solvent is undesirable, because completely dry powder burns too fast for satisfactory use as a propellant, and also because completely dry powder is so hygroscopic that it changes rapidly in moisture content and in ballistic properties when exposed to air.

The solvent is recovered from the powder by either of two methods. In the older method the powder is placed in a

The primary object of this work is to
show that the system of thought which
has been called "idealism" is not a
philosophy, but a method. It is a method
of thought, and it is a method which
has been used by many philosophers.
It is a method which has been used
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philosophers, and it is a method which
has been used by many philosophers.

closed system and air, at about 60° C., is circulated through it. The warm air removes most of the solvent from the powder, and the solvent is then removed from the air by cooling or by scrubbing with a suitable solvent. The process requires careful control, since the powder, on drying, tends to form a surface skin through which further passage of the solvent from the interior is very slow.

The newer method of solvent recovery is known as "water drying". In this process, warm water is used instead of air. The water causes the formation of microscopic cracks and pores on the surface of the powder, thus preventing the formation of the surface skin and allowing the solvent to pass from the interior of the grain into the water. The alcohol and ether pass into the water because they are more soluble in water than in powder. Thus the process is really one of extraction. In addition to more effective drying, this process reduces the warping customarily suffered by air-dried powder.

When the solvent has been sufficiently removed, the powder is taken out of the water, and the surface water is removed in a dryer. The finished powder contains about 3 per cent of volatile matter in the interior of the grain and about 1 per cent of surface water. Most of this is actually contained in the microscopic cracks and pores on the surface.

The amount of water held on the surface is extremely important in affecting the stability of the powder. The amount of water should be such that there is little tendency

for the moisture to evaporate in dry weather or for the powder to take up water during humid weather.

After drying, the powder from several batches is blended to produce a large quantity of essentially uniform powder. Such a quantity is called a "lot". The powder from each lot is generally kept together and assigned to be used by the same ship or battery.

After blending, the powder is stored in metal-lined boxes sealed with rubber gaskets. Every effort is made to keep the containers watertight, to avoid the effects of changing humidity.

Stability of Smokeless Powder

Even pure nitrocellulose, in either the colloided or uncolloided state, tends to decompose slowly on standing, with the formation of nitric oxide and nitrogen dioxide. The rate of decomposition rises with the temperature; the reaction is accelerated by high humidity. In the presence of acid the rate of decomposition is very greatly increased. Nitrocellulose that has not been freed completely from sulfate esters of cellulose is much less stable than the thoroughly purified material. The sulfate esters hydrolyse more rapidly than the cellulose nitrate itself, and the traces of sulfuric acid set free by the hydrolysis catalyse the decomposition. The nitrate esters of hydrocellulose and oxycellulose also tend to make the powder unstable; they decompose readily to form oxides of nitrogen that can react with

any moisture present to form acids that catalyse the decomposition of the true nitrocellulose.

Although well purified nitrocellulose is rather stable and does not begin to break down readily at room temperature, a small amount of decomposition does take place within a relatively short period of time. The oxides of nitrogen produced by this decomposition attack the nitrocellulose very rapidly, causing further decomposition. Thus, if these oxides are not removed, the decomposition is "auto-catalytic" and its rate increases rapidly, causing considerable decomposition in a short time. For this reason there must be added to the smokeless powder some compound which will react with the oxides as fast as they are formed, tying them up as some compound which does not further the decomposition. Such an additional compound is called a stabilizer, and powder to which it has been added is said to be stabilized.

Stabilizers

There are two important requirements for a good stabilizer in addition to the obvious one that it must react with the oxides of nitrogen formed by the decomposition of nitrocellulose.

First, neither it nor the product of its reaction with the oxides of nitrogen should react with the nitrocellulose. Thus the use of an alkali as a stabilizer is not feasible, because both the alkali and the nitrates and nitrites formed from it react very rapidly with nitrocellulose. (1)

Second, neither the stabilizer nor its products should destroy the homogeneity of the powder. Calcium carbonate, which is a good stabilizer for dynamite, cannot be used for smokeless powder because it is insoluble and remains as a finely divided solid in the powder. Urea, which otherwise is a very good stabilizer, cannot be used because it produces bubbles of nitrogen gas in the powder.

The stabilizer should also be relatively cheap, and both it and its products must be themselves stable.

Stabilizers have been used in smokeless powder ever since its first manufacture in France in 1884. The first substance used was amyl alcohol (2), which reacts with the oxides of nitrogen to form esters, amyl nitrite and amyl nitrate. These esters are in turn attacked by the oxides, and break down, releasing nitric and nitrous oxides, and at the same time the amyl radical is oxidised to valeric acid. The presence of valeric acid can readily be detected by its odor, and its presence was taken as evidence that the amyl alcohol was exhausted and the powder no longer stable. Since each molecule of amyl alcohol reacts with only one nitrogen, which it later gives up, amyl alcohol is a very poor stabilizer. Its use was abandoned, but not until two French warships had been destroyed by explosions attributed to spontaneous inflammation of the powder in their magazines. The Italians used aniline as a stabilizer, but since aniline itself attacks nitrocellulose, it makes a very poor stabilizer and its use was soon discontinued.

There are two main reasons why the Government should not be too hasty in making a decision on the proposed Bill. The first reason is that the Bill is very new and it is not yet clear what its effect will be. The second reason is that the Bill is very important and it is not yet clear what its effect will be.

By far the most important stabilizer is diphenylamine, which was used as early 1909 and is still the standard in most countries, including the United States.

The only substance which can compete with diphenylamine as a stabilizer is "Centralite", a trade name for any of several alkyl-substituted diphenyl ureas, the most usual being symmetrical diethyl diphenyl urea. However the centralites are used chiefly as solvents and coatings. In this paper diphenylamine and centralite will be discussed in detail, followed by a list of other compounds which have been used or proposed and a discussion of the comparative stabilization powers of the various compounds.

Diphenylamine

Diphenylamine is by far the most important stabilizer for smokeless powder, although it is generally considered that centralite is actually a better stabilizer.

The qualities of diphenylamine as a stabilizer were first established by M. Marquoyrol in a series of researches lasting fifteen years (3). Samples of smokeless powder containing up to 10 per cent of diphenylamine were heated at five different temperatures for periods up to 4083 days, and samples were removed from time to time for analysis of the nitrogen content of the nitrocellulose. Up to that time it was generally considered that smokeless powder decomposed at a rapid and uncontrollable rate. Marquoyrol's tests established the fact that nitrocellulose is essentially stable and loses stability only

The first step in the investigation is to determine the nature of the problem. This is done by a careful study of the facts and a determination of the points at issue. The next step is to collect the material which is necessary for the solution of the problem. This is done by a search of the literature and by the use of other sources of information. The third step is to analyze the material which has been collected. This is done by a comparison of the facts with the principles of the science which is being investigated. The fourth step is to synthesize the results of the analysis. This is done by a comparison of the results with the principles of the science which is being investigated. The fifth step is to draw conclusions from the results. This is done by a comparison of the results with the principles of the science which is being investigated.

Conclusions

The results of the investigation are as follows: The first conclusion is that the problem is a complex one. The second conclusion is that the material which has been collected is sufficient for the solution of the problem. The third conclusion is that the analysis of the material has shown that the principles of the science which is being investigated are applicable to the problem. The fourth conclusion is that the synthesis of the results of the analysis has shown that the principles of the science which is being investigated are applicable to the problem. The fifth conclusion is that the drawing of conclusions from the results has shown that the principles of the science which is being investigated are applicable to the problem.

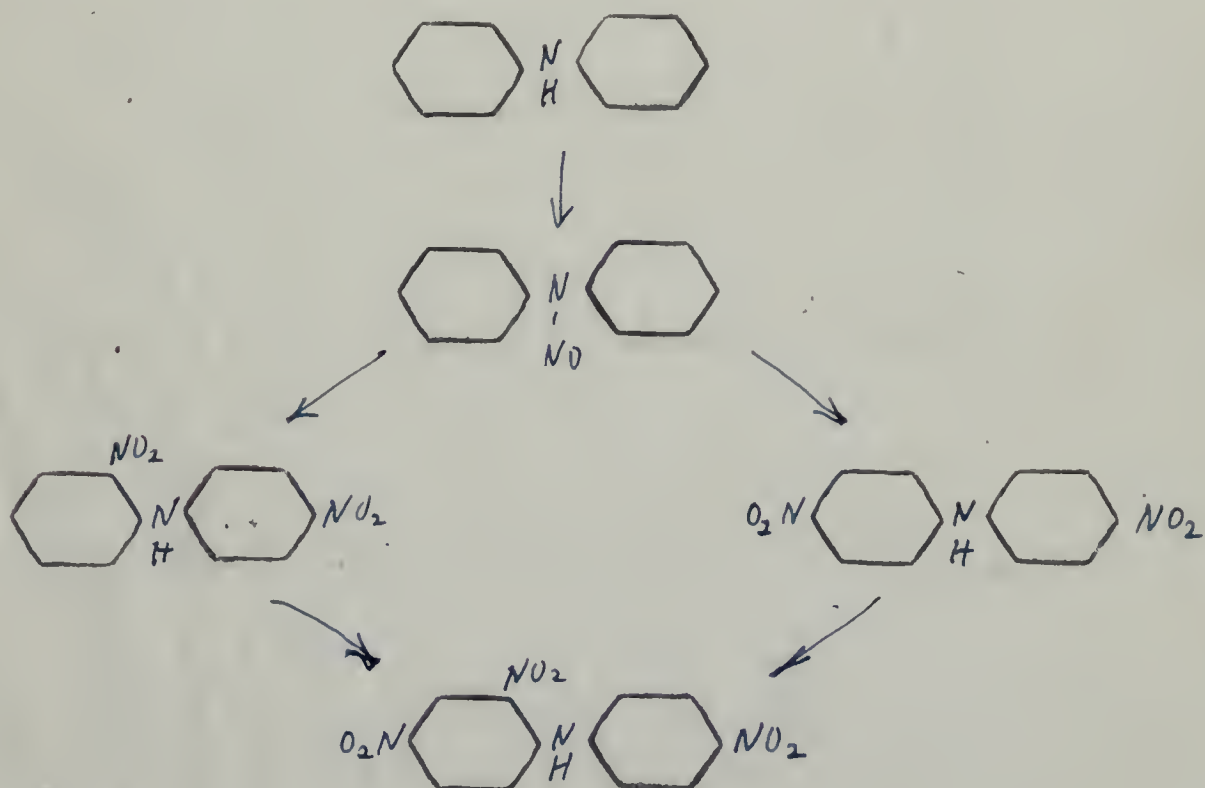
when in contact with slight amounts of its decomposition products. He showed that the first reaction product of diphenylamine is diphenylnitrosamine, which is itself a better stabilizer than diphenylamine. This is due to the fact that nitrosamine is a gelatinizer for nitrocellulose, and remains intimately mixed with it, whereas diphenylamine does not. However at elevated temperatures the nitrosamine has very poor stabilizing power.

These tests also showed that the effect of temperature is very important on the action of a stabilizer, since some of the reaction products may themselves be unstable at certain temperatures. Therefore any test for stabilization should be run at at least two temperatures. These observations in regard to the effect of temperature were confirmed by other researchers (4) (5) who also found that the presence or absence of oxygen and the amount of moisture present in the powder also materially affected the results.

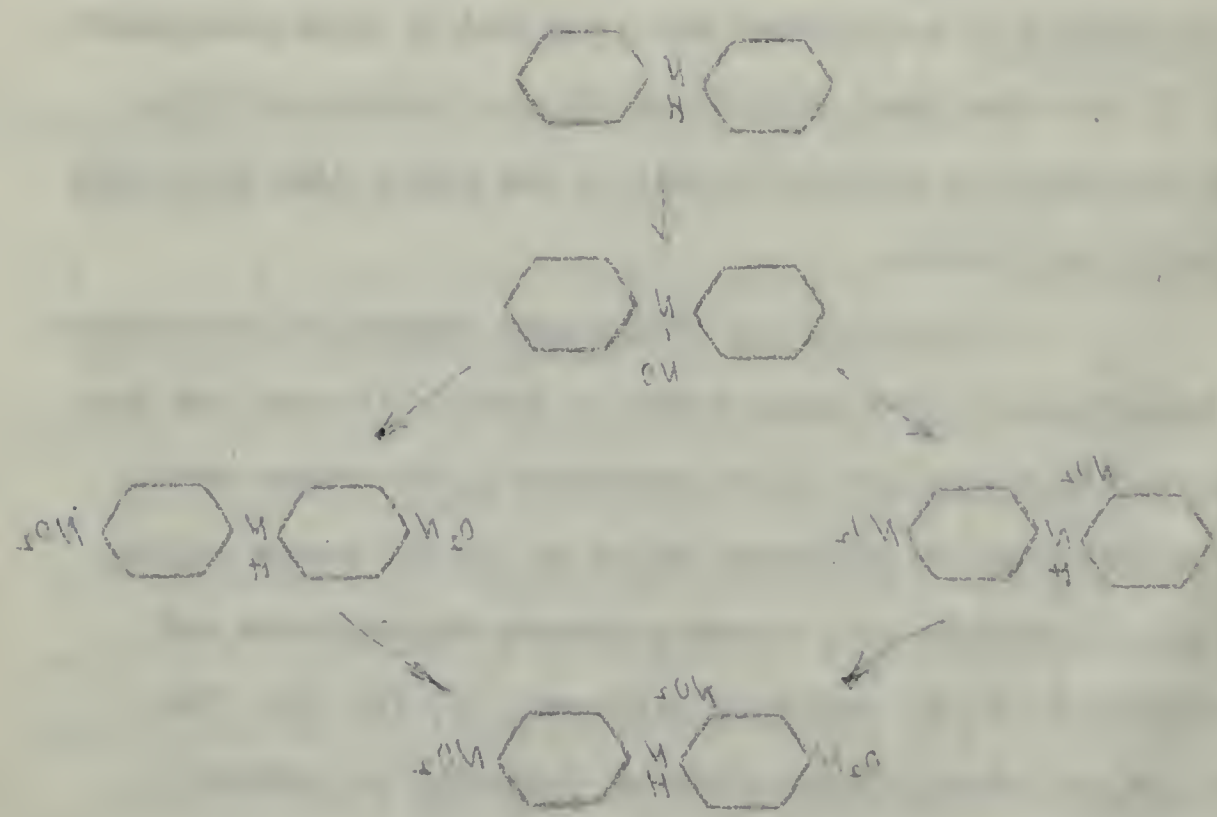
Marqueyrol and others have studied the derivatives of diphenylamine which cause powder to darken with age, and have concluded that they are due to impurities in the ether used in the powder or to the oxidizing action of the air during drying, and are not products of a reaction between diphenylamine and nitrocellulose or the oxides of nitrogen. (6) (7) (8). The principal oxidation product producing darkening is diphenyl dihydro phenazine.

The transformations undergone by diphenylamine as a result of the decomposition of the powder have been studied

by several investigators and seem to be fairly well established. The chief work in this field was done by Davis and Ashdown at M. I. T., working under a contract for the U. S. Army. (9) (10) They prepared all the compounds which might be expected to be formed by nitration of diphenylamine and devised color tests to indicate the presence of each of them, as well as methods of separating each from mixtures of one another and nitrocellulose. These separations and tests were applied to diphenylamine-stabilized powders in various stages of decomposition, the most advanced being a powder that had been giving off fumes for several months. These tests indicate that the reactions are as follows:

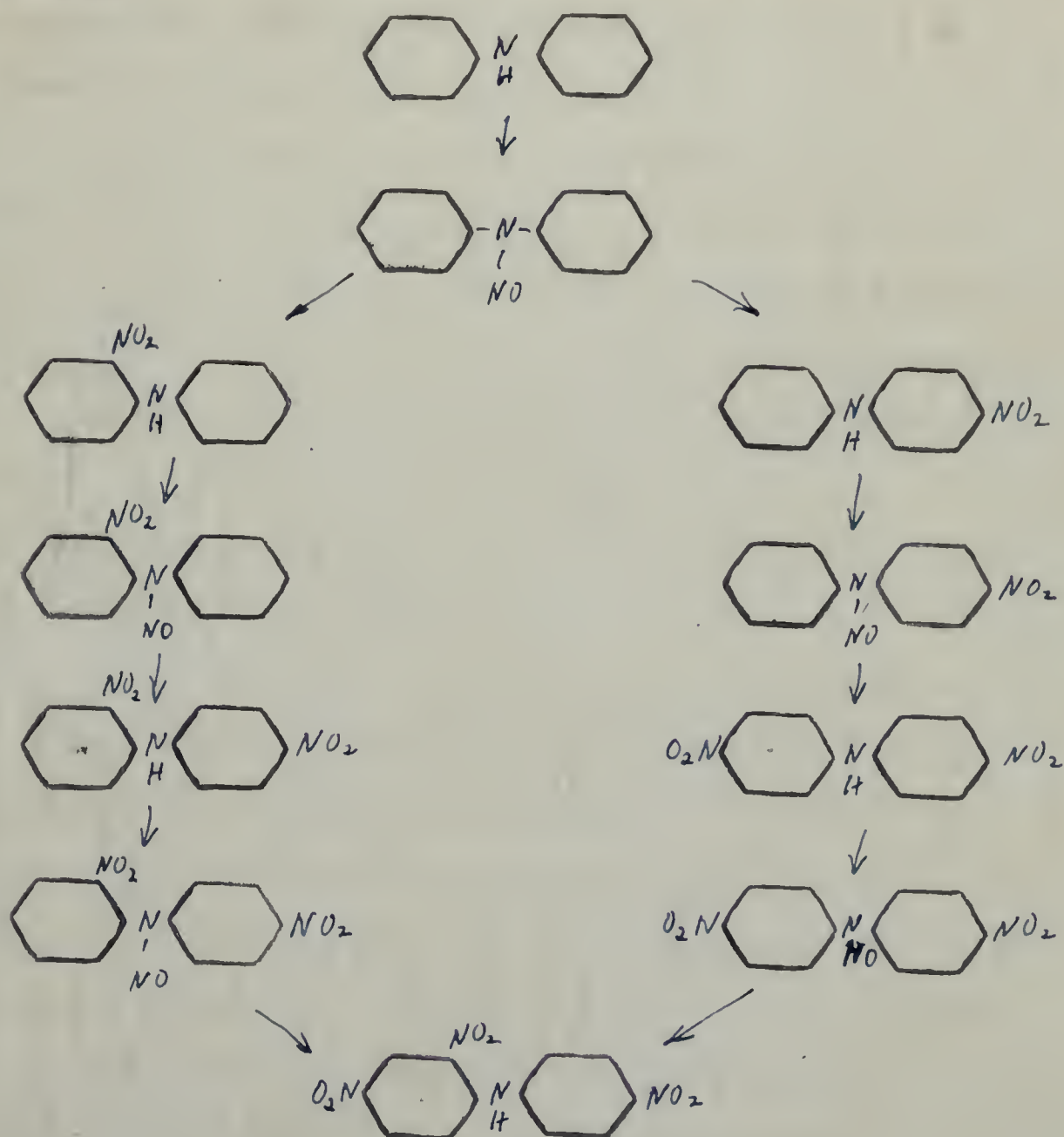


in the present investigation the only way to be sure of this is to separate the
the whole lot in this state and then to separate it
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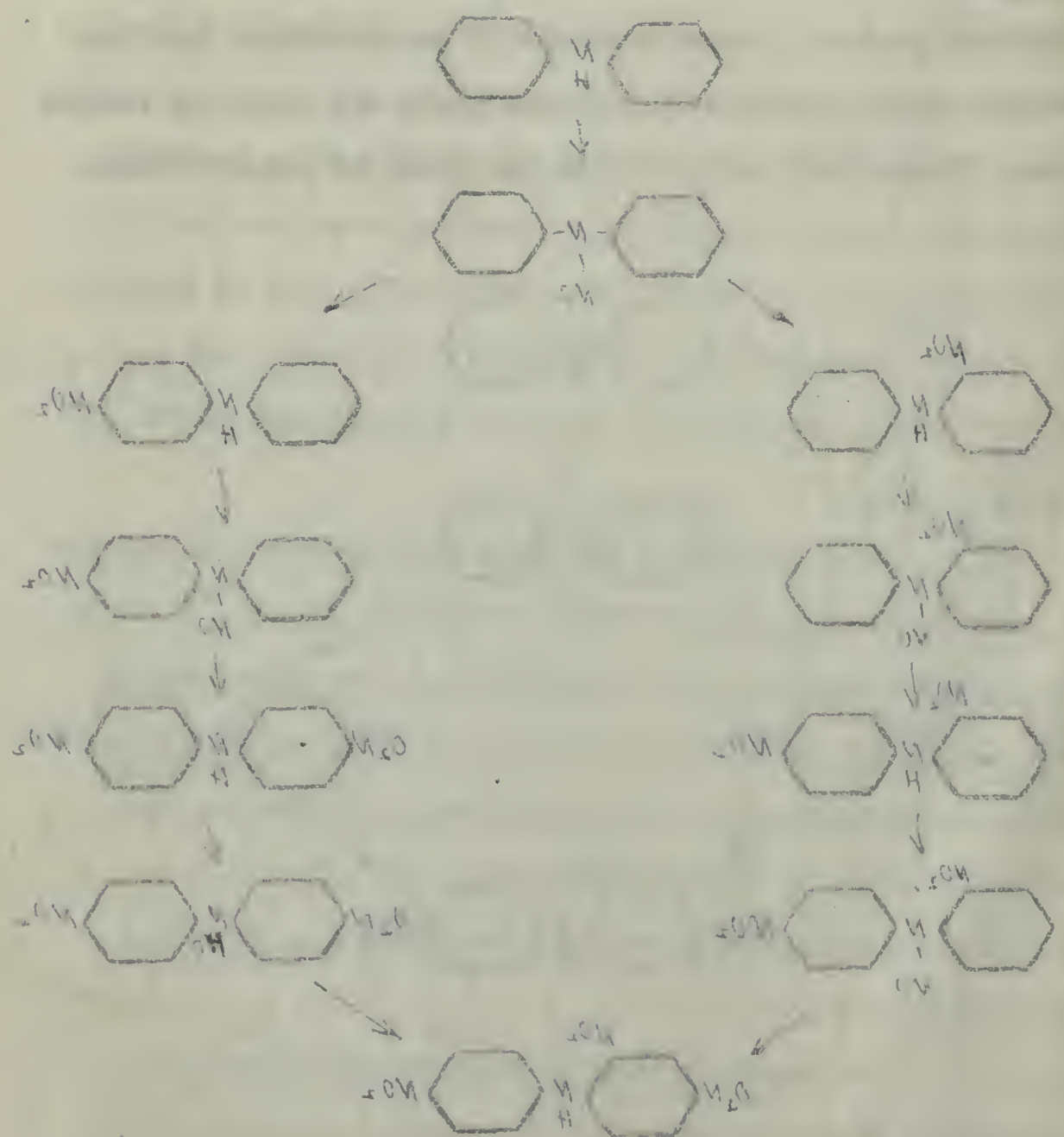


The last product formed, 2-4-4' trinitrodiphenylamine, might be expected to undergo further nitration to the 2-4-2'-4' tetranitro compound, but rather exhaustive attempts to isolate this compound were not successful.

Becker and Hunold, (11), confirm the fact that the tetranitro product is not formed. They also isolated several more intermediate compounds. Their proposed reactions are as follows:



The first reaction is the formation of the
 radical, which is initiated by a suitable radical source in the
 presence of a suitable solvent and at a suitable temperature.
 It is known that the radical is formed by the reaction of
 the radical source with the monomer.
 The radical then reacts with the monomer to form a
 dimer radical, which then reacts with another monomer to form
 a trimer radical, and so on, until a polymer of the desired
 molecular weight is formed.



The two mechanisms lead to the same end product, a trinitro derivative. The fact that diphenylamine takes up three nitro groups per molecule is one of the reasons that the compound is such a good stabilizer.

Becker and Hunold also measured the relative time required for the formation of the various compounds from powder containing diphenylamine, which was kept at 100° C. The nitrosamine was detected even before heating, the mononitro compound after one day at the elevated temperature, the dinitro after two days and the trinitro after four days.

They also tested the stabilizing power of the various intermediates by preparing powders containing each of these compounds. The relative values were as might be expected, except that the last product, the trinitro compound, was a better stabilizer than the compounds immediately preceding it, the dinitro diphenylnitrosamines. Since neither of these actually takes up any more nitrogen, it is hard to see how either can act as a stabilizer. No explanation was offered.

There is some evidence that the reaction is not as simple as the above discussion might indicate. The effect of temperature has been largely ignored in both the above experiments, but other workers have found that the reaction is apparently different at different temperatures. It was found (12) that stabilized powders decomposed at a rate which was only one-fifth to one-sixth that of unstabilized powder at 50° C., but at 77.5° C. its reaction rate was one-third that of the unstabilized powder.

The first section of the report is devoted to a description of the general situation of the country. It is found that the country is a large one, and that the population is very small. The climate is very hot, and the soil is very fertile. The country is very rich in minerals, and there is a great deal of gold and silver. The country is very rich in timber, and there is a great deal of iron and copper. The country is very rich in oil, and there is a great deal of coal. The country is very rich in fish, and there is a great deal of game. The country is very rich in all kinds of natural resources, and there is a great deal of room for development.

This would indicate either that the reactions are different at different temperatures, or that the method of testing is inaccurate. The low-temperature test may not indicate the true velocity of decomposition.

It was also found (13) that a catalyst was necessary to carry out the reaction between diphenylamine and oxides of nitrogen in the laboratory. Chlorides and copper salts were used as catalysts. It is supposed that the small amounts of copper salts present in smokeless powder from the various manufacturing containers act as catalyst when the reaction occurs in powder.

It has also been observed that the purity of the diphenylamine and of the nitrocellulose affect the stability.

(14) Powders made in 1912 with normally stabilized nitrocellulose and purified diphenylamine showed no loss of stability when tested after twenty years storage at room temperature, while powder manufactured during the first World War, using rapidly stabilized nitrocellulose and technical diphenylamine, showed marked losses of stability in fifteen years.

In this connection it is interesting to note that it is possible to restabilize powder with diphenylamine. The process (15) is performed by softening the powder in alcohol, without altering the grain size, and then re-impregnating with diphenylamine in alcohol solution.

Powder which has been stabilized with diphenylamine may be tested for stability and suitability for further use rather easily. A powder is considered unfit for further

This work is intended to show that the conditions are different at different temperatures, so that the effect of heating is to increase the rate of the reaction.

It was also found that the rate of reaction was increased by the addition of a small amount of sodium chloride and water. It is suggested that the small amount of water which is present in the reaction mixture from the time the reactants are mixed is sufficient to cause the reaction to proceed. It is also suggested that the effect of the

temperature is to increase the rate of reaction. It is suggested that the rate of reaction is increased by the addition of a small amount of sodium chloride and water. It is suggested that the small amount of water which is present in the reaction mixture from the time the reactants are mixed is sufficient to cause the reaction to proceed. It is also suggested that the effect of the

of reaction is to increase the rate of reaction. It is suggested that the rate of reaction is increased by the addition of a small amount of sodium chloride and water. It is suggested that the small amount of water which is present in the reaction mixture from the time the reactants are mixed is sufficient to cause the reaction to proceed. It is also suggested that the effect of the

storage if all of the diphenylamine and the diphenylnitrosamine have been exhausted. These compounds may be detected in an alcohol extract of the powder by simple color tests as follows:

If diphenylamine is present, a strip of filter paper on which an alcoholic extract of the powder has been allowed to dry is colored blue by a drop of ammonium persulfate. Also, if the extract contains diphenylamine it is colored blue by the addition of a few drops of a saturated solution of ammonium persulfate. Diphenylnitrosamine gives no color with ammonium persulfate, but imparts an intense blue color to a few milliliters of cold concentrated sulfuric acid.

Centralite

The first centralite was symmetrical dimethyl diphenyl urea. It was called centralite because it was developed at the Central War Laboratory in Germany. The ethyl compound, symmetrical diethyl diphenyl urea, usually called Centralite No. 1, is now more common; the methyl compound is now called Centralite No. 2.

The reaction of centralite with oxides of nitrogen has also been studied rather intensively, but opinion as to the nature of the reaction differs. One belief is that the reaction is simple nitration, forming first a dinitro compound with nitro groups substituted in the para positions of the two phenyl rings, and finally a tetranitro compound with two ortho and two para positions substituted (16). Another theory is that the centralite molecule is broken up, forming p-nitro phenyl ethyl

It is recommended that the following be done:

There is also a small amount of the same material in the collection of the British Museum.

The first model is the experimental design. It is the most common and is the most difficult to develop. It is the most difficult to develop because it is the most difficult to develop.

For the purpose of providing a more complete and accurate picture of the situation in the field, the following information is being provided:

nitrosamine. (17) In either case, it should be noted that one centralite molecule takes up four nitro groups, which is one more than diphenylamine can absorb.

Other Compounds

Many other compounds have been used, or at least proposed, as stabilizers. Not much is known about the reactions they undergo, but a great many comparisons have been made as to the relative powers of stabilization. Some of the more important suggested substances are:

acardite (assymmetrical diphenyl urea)

alpha naphthyl urethane

camphor

carbazole

diamyl phthalate

diphenylbenzamide

ethyl oxinilate

mucic acid

naphthalene

nitro naphthalene

phenanthrene

potassium oxinilate

petrolatums of various kinds

phthalide

substituted urethanes

saccharic acid

tartaric acid

Mr. J. H. Bates is listed as being married at 1907, however, it
must have been before 1906, because after 1906 he was attending college.
He was born in 1884.

triacetate of methyl trimethylol methane (18)

triphenylamine

Comparison of Stabilizing Power

Many workers have made comparisons of the stabilizing power of various groups of the compounds listed above. However it is rather difficult to integrate the results, since methods differed widely and since each worker compared only a few compounds. The results of some of the more important experiments are given below:

Marqueyrol, in his work mentioned above, also made comparisons of the stabilizing power of several compounds. These included amyl alcohol, diphenylamine, nitronaphthalene, naphthalene, diphenyl benzamide, diphenyl nitrosamine, and carbazole. He, of course, concluded that diphenylamine was the best stabilizer, and it was his work that first promoted the use of this compound. However, he found that for some temperatures the benzamide was better, and he also found that carbazole, while not as good a stabilizer as diphenylamine, has less direct action on the nitrocellulose at high temperatures, and therefore can be used in larger quantities with safety.

Giua and Guastalla (19) ran comparative tests on several compounds. They concluded that the compounds under consideration could be arranged in order of decreasing stabilizing effect as follows:

Diphenylamine

Centralite

THE EFFECT OF THE

and various other points of the
anatomical system of the human body
which, however, it is not possible to discuss in detail
and which will not be dealt with in this paper.
The results of the work of the author
concerning the effect of the

operation, in the case of the
this operation of the abdominal cavity in several cases.
From the point of view of the anatomical, physiological,
topographical, clinical, and pathological aspects, and
the results of the operation, the author has found that
the best results are obtained when the operation is performed
in the case of the abdominal cavity, and in the case of the
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Aniline

alpha Naphthylurethane

Ethyl Oxinilate

Potassium Oxinilate

Phthalide

M. Tonegutti, (20) (21), found that diphenylamine and centralite were of equal power and were the best stabilizers of all he tested. Disubstituted urethanes were good stabilizers when mixed with acardite, but not alone, while phthalide and diamyl- and dibutyl-phthalates had no stabilizing action at all. Substances that are both stabilizers and gelatinizers gave very good results when mixed with substances which are stabilizers only, producing better stabilization than either substance used alone. Phenanthrene gave very good results on nitroglycerine powders. He concluded that diphenylamine is the best stabilizer for double-base powders, but acardite is the best for single-base powders.

Tonegutti also compared the stabilizing power of various petrolatums, since these were being seriously considered at that time. (22) As might be expected, it was found that those having the highest degree of unsaturation (as shown by the bromine number) were the best stabilizers.

R. Dalbert (23) compared powders containing 8.75 per cent of centralite with powders in which 2 per cent of the centralite had been replaced with either diphenylamine or carbazole. In each case, the straight centralite was the best,

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the carbazole being the worst.

Dalbert also studied the action of triphenylamine as a stabilizer, comparing its action to that of diphenylamine.

(24) Powders containing two and five per cent of triphenylamine were compared with similar powders containing diphenylamine. The two-per cent powders showed similar action when heated to 100° C. but powder containing five per cent of triphenylamine showed less denitration than the corresponding diphenylamine powder. No nitroso compound was formed from the triphenylamine, the first product being a mononitro compound. These tests seem to indicate that triphenylamine might make a superior stabilizer, but apparently no further work has been done towards confirming this.

Krauz and Majrach considered the action of di- and tri- carboxylic acids, using tartaric acid as typical. Tartaric acid took up two nitro groups, forming dinitro tartaric acid. This compound when heated in aqueous solution decomposed into carbon dioxide, nitrogen trioxide, nitrogen, and a small amount of carbonic acid. If heated dry, the gases varied with temperature, glyoxalic acid being left in the solid residue. (25)

The same two workers also studied the nitro esters of other dicarboxylic acids, namely glutaric, mucic, and saccharic. These were found to act very much like tartaric acid, and to be better stabilizers than tartaric acid. (26)

Desmaroux (27) studied the comparative stabilising effects of camphor and centralite, and concluded that camphor was

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(10) The Commission has not yet received any information regarding the activities of the group in the United States.

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From a late, unpublished manuscript, it is known that the author of the "The Great Gatsby" was a man named Jay Gatsby. He was a wealthy man who had been in the army during the First World War. He was a very successful businessman and had made a fortune in the oil industry. He was a very charming man and was very popular with the women of the East Coast. He was a very successful man and was very popular with the women of the East Coast. He was a very successful man and was very popular with the women of the East Coast.

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as good as centralite, at least for periods up to 600 days, which was the longest test conducted.

Testing for Stability of Powder

No really satisfactory method of testing the stability of smokeless powder has as yet been devised. For research problems, such as comparing the stabilizing effect of various substances, the reduction in nitrogen content is taken as a measure of instability. Thus to compare two stabilizers, powders containing each are prepared, and rather large samples of each kept under carefully controlled conditions of temperature and humidity for a long time. From time to time, samples of each are withdrawn and analysed for nitrogen, the powder which has lost the least being considered the better stabilized. This method presents several difficulties and is really not very satisfactory. The nitrocellulose must be removed from the stabilizer and its products and tested for its nitrogen content. This presents difficulties and the method employed varies with the type of powder and the stabilizer. In addition, as has been mentioned before, the temperature plays an important part in the effective stability, some substances acting as very good stabilizers at one temperature but being very poor at other temperatures either higher or lower. Accordingly, such tests should be run at several temperatures.

Several methods have been used for testing stability without waiting for the actual decomposition to occur, as in the above tests. These are usually referred to as

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"heat tests". The two most common of these in this country are the 65.5° C. KI starch test and the 134.5° C. methyl violet test.

In the KI starch test, the powder samples are heated in test tubes at 65.5° C. Within each tube, a strip of KI starch paper, spotted with a 50 per cent aqueous solution of glycerine, is hung from a platinum hook. The tubes are stoppered with cork. The tubes are examined constantly and the time required for the first appearance of color on the paper is reported. Specifications in the United States call for at least 35 minutes before the first appearance of color.

In the methyl violet test, long tubes of heavy glass are used. They are closed loosely with notched corks, and are heated for almost their whole length in a bath at 134.5° C. The sample occupies about two inches of the lower end of the tube, and strips of methyl violet paper are placed about one inch above the sample. Times are noted for the paper to be turned completely to a salmon-pink color, for the first appearance of red fumes, and for explosion. Explosion usually does not occur for about five hours.

It will be noted that neither of the above gives a true indication of stability, since they measure the time for the self-catalyzed reaction in an atmosphere of air or red fumes. They thus serve only to compare the stability of powders which are similar in other respects. For true observations of stability, a heat test under vacuum is necessary.

Effects of Temperature and Humidity on Stability

If smokeless powder is exposed to a humid atmosphere, it will absorb moisture slowly. Conversely, it will give up moisture to a dry atmosphere. The extent of both of these is dependent on the amount of surface moisture present originally in the powder, as mentioned above. The hygroscopicity also seems to depend on the total amount of nitrocellulose present, so that double base powders are less hygroscopic than straight nitrocellulose powder.

The amount of moisture present has a very marked effect on the stability. In one experiment a powder was exposed to a saturated atmosphere for three months at 50° C. After this exposure, it was kept at 65.5° C. in a closed container, red fumes appearing after nine days. The same powder, unexposed to the humid atmosphere, took 540 days to produce red fumes under the same conditions. (28)

Changes in temperature and humidity affect the stability of powder in another fashion, also. As the powder takes up moisture, the water and volatile matter in the powder move inward from the surface toward the interior. If the same powder then loses water, due to a change in conditions, this water moves outward. Thus there is a constant shifting of the liquid within the powder. This tends to break up the structure of the grain and promote decomposition.

Smokeless powder deteriorates much more rapidly at high than at low temperatures. This is due partly to the

acceleration of the decomposition reaction of nitrocellulose and partly to the fact that the stabilizer also decomposes at high temperatures. Diphenylnitrosamine decomposes very easily as the temperature is raised, and hence the stability of diphenylamine powders decreases rapidly.

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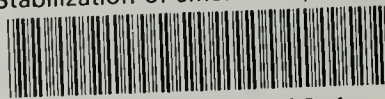
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